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METHOD FOR SEPARATING A KRYPTON-XENON CONCENTRATE
AND A DEVICE FOR CARRYING OUT SAID METHOD

FIELD OF THE INVENTION

5 The invention relates generally to cryogenic engineering. More specifically, the invention pertains to refining and separating a krypton-xenon concentrate obtained at air-fractionating installations, which concentrate can be used in chemical and gas and oil producing industries.

10 **BACKGROUND OF THE INVENTION**

 Known in the art is a method for refining and separating a krypton-xenon concentrate comprising preparing the krypton-xenon concentrate using a method of low temperature rectification from a weak, pre-purified of hydrocarbons, krypton-xenon mixture, refining the krypton-xenon concentrate to remove fluorine- and/or chlorine-
15 containing impurities and subsequently dividing the matter into high-purity krypton and high-purity xenon in a rectifying column. Purification of the krypton-xenon concentrate to remove fluorine- and/or chlorine-containing impurities in the known method is provided through chemical adsorption at a temperature comprised predominately between 450 and 550°C on a solid adsorbent comprising, for the most part, more than 50% of
20 phyllosilicates. Carbon dioxide and water are formed, which are removed by absorption of the carbon dioxide and the water in one of two reversing absorbers using molecular sieves, and removal of oxygen traces by contacting with a copper-nickel catalyst.

 The known method has drawbacks with regard to the high energy capacity and high specific quantity of metal required, brought about by the use in cryogenic production
25 processes of high temperature processes. Further, it is impossible to obtain particular high purity krypton and xenon in one column simultaneously.

 The closest to the present invention, in terms of technical essence, is an adsorption-rectification method for separating gases with the use of freezing steps providing for liberating xenon and krypton from a gas mixture containing krypton, xenon,
30 argon, and nitrogen. According to the conventional method, from a carbon dioxide and moisture pre-purified gas flow, the xenon is absorbed in a silica gel absorber, with the

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remaining gas mixture directed first to a rectifying column for preliminary krypton separation and then to a krypton column. The Xenon fraction is separated out, while recovering the absorber, and is intermittently directed to a nitrogen-cooled freezing apparatus where, while freezing the xenon and krypton, an appreciable portion of
5 nitrogen is removed from the fraction, with an admixture of krypton, adding it to the gas flow at the inlet of the column for krypton pre-separation, while a xenon concentrate obtainable after a cryoresidue has been fused, is purified to remove nitrogen/krypton remainders in the xenon column.

The drawbacks of the known method are its discontinuity associated with the use
10 of a freezing apparatus being filled with xenon fractions at regular intervals, additional expenditures of a coolant and electric energy on the alternating freezing and heating of the xenon fractions. as well as the impossibility of obtaining particularly pure krypton and xenon, when starting with the presence in a base mixture of, for example, fluorine/chlorine-containing compounds.

Also known is an apparatus for purifying and separating a krypton-xenon
15 concentrate, comprising an outfit-pipeline-connected low-temperature rectifying column for producing a krypton-xenon concentrate, a vessel filled with a solid sorbent containing phyllosilicates, for removing fluorine- and/or chlorine-containing impurities from the concentrate at a temperature comprised between 450 and 550°C, a pair of reversing
20 absorbers, a reaction vessel with a copper-nickel catalyst, and a rectifying column for the production of high-purity krypton and xenon. The device is disadvantageous in that it has a high energy capacity and a high specific quantity of metal, and because of the impossibility of obtaining in one column simultaneously particularly pure krypton and xenon.

Also known is a device for separating gases, comprising two adsorbents filled
25 with molecular sieves, a silica gel adsorbent, a xenon freezing means, a preliminary krypton separation rectifying column, and krypton and xenon rectifying columns connected via pipelines with the outfit. The device is disadvantageous with respect to its discontinuity of operation associated with the use of freezing means intermittently filled
30 with xenon fractions, additional expenditures of a coolant and electric energy in cooling and heating the freezing means as well as the impossibility of obtaining particularly pure

krypton and xenon, when starting with, for example, fluorine- and/or chlorine-containing impurities in a base mixture.

SUMMARY OF THE INVENTION

5 An object of the invention is to enhance the efficiency of particular pure krypton and xenon by maximizing their maximal recovery from a base mixture.

 A method for separating a krypton-xenon concentrate purified from hydrocarbons comprises separating a krypton-xenon concentrate flow in a preliminary rectifying column to form a krypton fraction flow and a xenon fraction flow, delivering and
10 separating the krypton fraction flow in a production krypton column to form a production krypton flow and a blowing gases flow of the krypton column, delivering and separating the xenon fraction flow in a production xenon column to form a production xenon flow and the blowing gases flow of the xenon column. A distinguishing feature of the invention is that the xenon fraction flow before the delivery and separation in the
15 production xenon column is further separated by rectification in an additional xenon column to form a purified xenon fraction flow, which is collected from an upper zone of the concentration part of the additional xenon column and fed for separation to the production xenon column, and a high-boiling admixtures flow. The krypton fraction flow, before the delivery and separation in the production krypton column is further separated
20 by rectification in an additional krypton column to form a purified krypton fraction flow being supplied for separation to the production krypton column, and an intermediate admixtures flow. The blowing gases flow of the krypton column is further separated by rectification in a krypton recovery column to form a low-boiling admixtures flow and a recovered krypton flow. The recovered krypton flow and the blowing gases flow of the
25 xenon column are directed for separation to the preliminary rectifying column and, more importantly, the rectifying columns are brought into operation with the krypton fed into the columns' contact space, and reflux is formed in? the evaporating condensers of the rectifying columns under conditions precluding formation of solids.

 An object of the invention is to enhance efficiency in producing particular pure
30 krypton and xenon as a result of their maximal recovery from a base mixture.

 This object is achieved by a device for separating a krypton-xenon concentrate

purified to remove hydrocarbons, and comprises a krypton-xenon concentrate line of flow feeding a preliminary rectifying column, a production krypton column with a blowing gases line of flow of the krypton column in communication via a krypton fraction line of flow with the preliminary rectifying column, a production xenon column with a blowing gases line of flow of the xenon column in communication via a xenon fraction line of flow with the preliminary rectifying column, each of which is provided with an evaporating condenser and a thermal converter. A distinction resides in that on the xenon fraction line of flow, a provision is made for an additional xenon column with a branch pipe in an upper zone of a concentration part complete with a feeding line of the additional xenon column, a purified xenon fraction line of flow connected with the branch pipe in the upper zone of concentration part, and a high-boiling admixtures line of flow. The additional xenon column line of flow is connected with the xenon fraction line of flow. The purified xenon fraction line of flow is connected with an outlet pipe of the purified xenon fraction and with a production xenon column feeding line. On the krypton fraction line of flow there is provided an additional krypton column equipped with an additional krypton column feeding line, a purified krypton fraction line of flow, and an intermediate admixtures line of flow. The additional krypton column feeding line is connected with the krypton column line of flow. The purified krypton fraction line of flow is connected with a production krypton column feeding line. On the krypton column blowing gases line of flow, additionally installed is a krypton recovery column provided with a krypton recovery column feeding line, a low-boiling admixtures line of flow, and a recovered krypton line of flow. The krypton recovery column feeding line is connected with the krypton column blowing gases line of flow and, along with this, the xenon column blowing gases line of flow, the high-boiling admixtures line of flow, the intermediate admixtures line of flow, the low-boiling admixtures line of flow and the recovered krypton line of flow are in communication with a purge collecting device and with the contact part of the preliminary rectifying column via pressure increasing devices. The concentration parts of the columns are further equipped with anticipatory assay nipples and the thermal converters are provided above the supply lines of the feeding flows of the columns at the distance $L=(0.4-0.8)H$, wherein H is the height of the concentration part of a respective column. The evaporating condensers of the columns

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comprise a closed space dividing the boiling surface of a coolant and a reflux vapors condensation surface filled with a working medium. The closed spaces of the evaporating condensers of the preliminary rectifying column, the production krypton column, the production xenon column, the additional krypton column and the additional xenon column are partially filled with packing, and the working medium is a mixture of oxygen and krypton while the working medium in the closed space of the evaporating condenser of the krypton recovery column is nitrogen, and the preliminary rectifying column is connected via a pipeline with a source of krypton.

The method for separating a krypton-xenon concentrate can be realized in the device schematically shown on the drawing.

BRIEF DESCRIPTION OF THE DRAWING FIGURE

Fig. 1 is a schematic illustration of a device for separating a krypton-xenon concentrate.

DETAILED DESCRIPTION OF THE INVENTION

A device (installation) comprises a preliminary rectifying column 1, an additional krypton column 2, a production krypton column 3, an additional xenon column 4, a production xenon column 5, a krypton recovery column 6, Each and every rectifying column has an evaporating condenser 7-1 to 7-6 at the top thereof and a still 8-1 to 8-6 at the foot thereof provided with an electric heating element 9-1 to 9-6. Still 8-1 of the preliminary rectifying column 1 additionally contains an evaporator 10.

Every evaporating condenser 7-1 to 7-6 has a closed space 12-1 to 12-6 to be filled with a working medium and the top portion of the surface of the closed space has heat interaction with a surface 13-1 to 13-6 of coolant boiling and the bottom portion - with a surface 14-1 to 14-6 for reflux vapors condensation. More, the middle portion of the closed space of the evaporating condensers 7-1 to 7-5 is filled with packing 15-1 to 15-5.

All the evaporating condensers have branch pipes communicated with liquid coolant inlet lines 16-1 to 16-6, and branch pipes communicated with coolant vapors outlet lines 17-1 to 17-6. The closed spaces of the evaporating condensers have branch

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pipes communicated with lines 18-1 to 18-6 for the delivery of a working medium in liquid state or with lines 19-1 to 19-6 for the delivery of the working medium in gaseous state as well as branch pipes connected by lines 20-1 of 20-5 allowing the working medium to run out into purge collection device 28. The preliminary rectifying column 1
5 has branch pipe in the middle portion thereof, connected by a pipeline via the evaporator 10 with a line 21 of a krypton-xenon concentrate flow (flow A), in the top portion - a branch pipe connected by a line 22 of a krypton fraction flow (flow B) with the branch pipe in the middle portion of the additional krypton column 2 and in the bottom portion, still 8-1 has a branch pipe connected by a line 23 of a xenon fraction flow (flow C) with
10 the branch pipe in the middle portion of the additional xenon column 4.

The additional krypton column 2 has a branch pipe in the top portion, connected by a line 24 of a purified krypton fraction flow (flow D) with the branch pipe in the middle portion of the production krypton column 3 and in the bottom portion, in still 8-2 - a branch pipe connected by a line 25 of an intermediate admixtures flow (flow E) via an
15 evaporator 26 and a pressure increasing device 27 with a branch pipe provided in the bottom portion of the contact space of the preliminary rectifying column 1 or downstream of the evaporator 26 with a purge collection device 28 or with the exit of the installation.

The production krypton column 3 has a branch pipe in the top portion, connected by a line 29 of a krypton column blowing gases (flow F) with a branch pipe in the middle
20 portion of the krypton recovery column 6 and in the bottom portion, in still 8-3, a branch pipe connected by a line 30 of a production krypton flow (flow G) via the evaporator 26 with the exit of the installation.

The additional xenon column 4 has a branch pipe in the top portion, connected by a line 31 of a purified xenon fraction flow (flow H) with a branch pipe in the middle
25 portion of the production xenon column 5, in the upper zone of a concentration part - a branch pipe connected with the line 31 by a line 44, and in the bottom portion in still 8-4, a branch pipe connected by a line 32 of a high boiling admixtures flow (flow I) via the evaporator 26 and a pressure increasing device 33 with a branch pipe positioned in the bottom portion of the contact space of the preliminary rectifying column 1 or downstream
30 of the evaporator 26 with the purge collection device 28 or with the exit of the installation.

The production xenon column 5 has a branch pipe in the top portion, connected by a line 34 of a xenon column blowing gases flow (flow J) with the purge collection device 28 or via a pressure increasing device 35 with a branch pipe provided in the bottom portion of the contact space of the preliminary rectifying column 1 and in the bottom portion, in still 8-5, a branch pipe connected by a line 36 of a production xenon flow (flow K) via the evaporator 26 with the exit of the installation.

The krypton recovery column 6 has a branch pipe in the top portion, connected by a line 37 of a low boiling admixtures flow (flow L) with the purge collection device 28 or via a pressure increasing device 43, with a branch pipe provided in the bottom portion of the contact space of the preliminary rectifying column 1 or with the exit of the installation, and in the bottom portion, in a still 8-6, a branch pipe connected by a line 38 of a recovered krypton flow (flow M) via the evaporator 26 with the purge collection device 28 or via a pressure increasing device 41 with a branch pipe provided in the bottom portion of the contact space of the preliminary rectifying column 1 or with the exit of the installation.

To bring a device into operation, a diagram provides for a source 39 of krypton which is connected by a krypton supply line 40 (flow N) with the preliminary rectifying column 1.

All the rectifying columns comprise thermal converters T1-1 to T1-6 for measuring liquid temperatures in a still, thermal converters T2-1 to T2-6 for measuring medium temperatures, positioned in the section of an upper (concentration) part above an inlet of flows A, B, C, D, F, H at a distance (L) making up 0.4 to 0.8 of the height (H) of the concentration part of a respective column, nipples A 1-1 to A 1-6 of an assay pipes outlet from the steam zone of the still, samplers A2-1 to A2-6 of a vapour phase outlet, positioned at the distance $L_1 = 0.5$ to 1.0m of the head of the concentration part and nipples M1 to M6 of a pulse pipe outlet toward pneumatic converters. Nipples A3—1 to A3-6 for the assay pipes outlet are likewise positioned on lines of flows B, D, F, H, J, L, respectively, and nipple A4-1 on the line of flow C. All the rectifying columns and low-temperature pipelines are contained in an insulating enclosure 11 and filled with a heat-insulating material; perlite powder, for example.

A method for separating a krypton-xenon concentrate is carried out in the

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following manner.

The vacuum pretreated contact spaces of rectifying columns 1 to 6 are supplied with a krypton flow (N) along the line 40 from the krypton source 39, maintaining a pressure after a reductor from 0.15 to 0.3 MPa, predominantly 0.2 MPa. At the same time
5 liquid nitrogen is supplied along lines 16-1 to 16-6 to the boiling surfaces of coolant 13-1 to 13-6 of evaporating condensers 7-1 to 7-6, the nitrogen being utilized as a coolant that boils under a pressure of from 0.11 to 0.15 MPa, and the generated steam is removed along lines 17-1 to 17-6. Upon completion of a step of freezing the boiling surfaces, which is characterized by an abrupt reduction in the amounts of the steam removed along
10 the lines 17-1 to 17-6, closed spaces 12-1 to 12-5 of evaporating condensers 7-1 to 7-5 are supplied with, as working medium, an oxygen-krypton mixture containing 40-90% of krypton in a gaseous state along lines 19-1 to 19-5 or in a liquid state along lines 18-1 to 18-5; closed space 12-6 of evaporating condenser 7-6 is supplied, as working medium, with gaseous nitrogen along line 19-6 or liquid nitrogen - along line 18-6. At the time of
15 supplying the oxygen-krypton mixture in the gaseous state, a mixture pressure is maintained from 0.2 to 0.7 MPa, predominantly 0.3 MPa. While feeding the gaseous nitrogen, the inlet pressure is maintained at 2.4 - 3.0 MPa, predominantly at 2.5 MPa. Upon condensation of required amounts of the working medium being determined according to a level in the lower portion of the surface of a closed space, its delivery is
20 terminated. While feeding the working medium in the liquid state, the steam generated in freezing is condensed in the upper portion of the surface of the closed space. Simultaneously with emergence of the working medium liquid in the lower portion of the surface of the closed space, there begins the condensation of krypton and a further freezing of the rectifying columns. With the liquid krypton originating appearing? in stills
25 8-1 to 8-6, the freezing process has stopped, electric heating elements 9-1 — 9-6 are supplied with electric power, and the columns are changed over to a cycle of "endless reflux" by way of changing the flow times of the coolant while maintaining in the closed space of the evaporating condensers, a pressure permitting to establish the operating pressure in the contacting space of the rectifying columns, on the one hand, and the
30 temperature of the surface of reflux vapours condensation above that of krypton's freezing point, on the other, thus preventing the ice from freezing over.

The krypton-xenon concentrate produced on air-fractionating installations, purified from hydrocarbons and incorporating krypton Kr, xenon Xe with admixtures, such as nitrogen N₂, oxygen O₂, argon Ar, neon Ne, helium He, hydrogen H₂, carbon oxide CO, tetrafluoromethane CF₄, hexafluoroethane C₂F₆, monofluorotrichloromethane (freon 11) CFC1₃, difluorodichloromethane (freon 12) CF₂Cl₂, to mention but few, is
5 supplied along line 21, substantially at a pressure of between 0.2 and 0,25 MPa into the preliminary rectifying column 1, in which the reflux is a krypton condensate. As a result of a rectification process in still 8-1 there is collected a xenon fraction containing all of the xenon and admixtures which are high boiling as regards to the krypton, for example
10 C₂F₆, CFC1₃, CF₂Cl₂, etc., as well as a little purposely maintained amount of krypton (2-5 vol.%) and at the head of the column — is the krypton fraction containing the krypton, admixtures which are volatile as regards the krypton and also CF₄ and other admixtures having a krypton approximating boiling temperature. The rectification process is conducted according to the indices of a pneumatic converter connected to nipple M1,
15 thermal converters T1-1 and T2-1, assays taken from nipples A1-1, A3-1, A4-1 and an assay taken from sampler A2-1, and thermal converter T2-1 mounted at the distance L= (0.4 - 0.8)H above a flow A inlet where H is here the height of the concentration part of the preliminary rectifying column, is present in a zone of concentrations maximum change and, therefore, is highly sensitive to a change in conditions, and the assay from
20 the sampler A2-1 is anticipatory for taking measures to preclude, for example, xenon uptake to a condensation surface.

In closed space 12-1, with the krypton content of 80 vol.%, the pressure is maintained at 0.25 MPa, a factor that ensures a minimal temperature difference, as to a tendency for krypton not to freeze up, being roughly 2K. This low pressure in a closed
25 space is ascribed to the use, as working medium, of a mixture of krypton and oxygen with the separation of components on packing 15-1, with the result that the boiling temperature of the mixture in the lower portion of the closed space exceeds the oxygen condensation temperature in an upper portion of the closed space by 18 K. Prevention of conditions for ice formation on the condensation surface 14-1 and also on condensation
30 surface 14-2 to 14-6 in other evaporating condensers prevents the possibility of an installation being stopped in connection with the filling-in of rectifying columns, taking

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the chill off and start-up thereof.

From the head of the preliminary rectifying column 1 along line 22, a krypton fraction flow is directed to the additional krypton column 1, where the reflux is a krypton condensate. Inasmuch as tetrafluoromethane CF_4 and other admixtures having, with the same pressure, a boiling temperature higher than a krypton boiling temperature are difficultly volatile with respect to the krypton, in combination with which they are concentrated in still 8-2 of the column and can be withdrawn from an installation on the line 25 of an intermediate admixtures flow via the evaporator 26 to be utilized as a target product. For example in using the krypton, as a filler gas, for window multiple glass units or directed to the purge collection device 28 or returned through the pressure increasing device 27 into the contact area of the preliminary rectifying column 1.

From the head of the column 2, a purified krypton fraction flow is withdrawn along the line 24, already devoid of admixtures which are difficultly volatile with respect to krypton and directed to the middle portion of the krypton production column 3 wherein the reflux is a krypton condensate. As a result of the rectification process the production krypton collects in still 8-3, which is taken out of an installation along the line 30 of a production krypton flow, and a krypton column blowing gases flow is withdrawn from the head of the krypton production column 3 along the line 29, which contains the krypton and all the relative-to-krypton volatile materials, and directed to the middle portion of the krypton recovery column 6. As mentioned above, in closed space 12-6 of evaporating condenser 7-6 nitrogen is present at a pressure of about 2,5 MPa and the krypton, in the contact space of the column. Therefore, on starting up the installation, the reflux in the krypton recovery column is a krypton condensate being formed on condensation surface 14-6 with no solids.

As a krypton column blowing gases flow is fed to a krypton recovery column, the pressure therein is increased, it is reduced to the former value by removing noncondensing gases along the line 37 of a low boiling admixtures flow and at the same time decreasing the nitrogen pressure in closed space 12-6, which is effected by increasing boiling surface 13-6 of a coolant by raising its level. While lowering the nitrogen pressure in closed space 12-6 to 0.2 to 0.25 MPa, the reflux in the krypton recovery column already consists of a mixture of low boiling liquids (N_2 , O_2 , Ar) while a

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krypton content in the line 37 of the low boiling admixtures does not exceed 0.3 vol.%. And the supply of the coolant to evaporating condenser 7-6 is transferred to line 16-6 directly into closed space 12-6 with the removal of coolant steam along line 20-6.

A low boiling admixtures flow M from the head of the krypton recovery column 6 is taken from an installation or directed to the purge collection device 28 or via a pressure increasing device 43 it is returned into the contact space of the preliminary rectifying column 1. From still 8-6 a flow H of recovered krypton is withdrawn via the evaporator 26, from the installation or directed to the purge collection device 28 or returned via pressure increasing device 41 to the contact space of the preliminary rectifying column 1.

From still 8-1 of the preliminary rectifying column 1, a xenon fraction flow C is directed through the line 23 to the middle portion of the additional xenon column 4 and, along with this, in closed space 12-4 of evaporating condenser 7-4, the pressure of an oxygen-krypton mixture is gradually increased to ~2.5 MPa, which is effected by reducing boiling surface 13-4 of 9 coolant by lowering its level. With a pressure reaching ~2.5 MPa on condensation surface 14-4 there forms xenon reflux and krypton becomes a noncondensing gas. As a result of the rectification process in still 8-4 all the admixtures are concentrated together with a part of xenon, which are present in a xenon fraction flow and have a boiling temperature higher than the xenon boiling temperature, including C₂F₆, CFC1₃, CF₂Cl₂ and so on, and so forth. From still 8-4 the high boiling admixtures flow I is withdrawn along the line 32 via the evaporator 26, from the installation as a final product. For example, using the xenon as a filler gas for window multiple glass units, or returned via the pressure increasing device 33 to the contact space of the preliminary rectifying column 1 or directed to the pure collection device 28.

From the head of the additional xenon column 4 along the line 31 or from the upper zone of the concentration part of the additional xenon column 4 along the line 44, the purified xenon fraction flow H containing xenon and krypton alone is directed to the middle portion of the production xenon column 5 wherein the reflux is a krypton condensate. As a result of the rectification process, production xenon gathers in still 8-5, which is withdrawn from an installation along the line 36 via the evaporator 26, and a flow of blowing gases of a xenon column K is withdrawn from the head of production xenon column along the line 34, which is directed to purge collection device 28 or

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returned via the pressure increasing device 35 to the contact space of the preliminary rectifying column 1.

On collection of purified fraction from the upper zone of the concentration part of the additional xenon column 4 along the line 44 in the additional xenon column, the
5 reflux is a krypton condensate, a factor that permits reducing the operating pressure of a krypton-oxygen mixture in closed space 12-4 of evaporating condenser 7-4 from 2.5 MPa to 0.2-0.25 MPa.

In the case of a need to stop an installation, all of the contents of the contact space of columns 1,2,3, upon evaporation, are let go across the columns 4 and 6 to proceed
10 along the lines 32 and 38, respectively, to the purge collection device 28; it is then withdrawn via the pressure increasing device 35 along the line 42, from the installation to a reservoir for subsequent treatment. On disposal of the contents of the contact space of the columns into the purge collection-device 28, a krypton-oxygen mixture is let out of closed spaces 15-1 to 15-5 of the evaporating condensers respectively along lines 20-1 to
15 20-5 whence it is directed from the installation, via the pressure increasing device 35 along the line 42, to a separate reservoir for subsequent purposeful use.

The claimed method and device for separating a xenon-krypton concentrate practically with any admixtures allow one to achieve a recovery index, as to krypton and xenon, of no less than 0.99995 with the contained admixtures in production krypton and
20 xenon of not greater than $10 - 10^{-11}$ **parts per volume**.

The claimed method for separating a krypton-xenon concentrate and a device for carrying out same make it possible to raise efficiency of obtaining highly pure krypton and xenon on account of their maximum recovery and the continuity of the processes.